4.6 The Sulphur Cycle

4.6.1 Introduction

The sulphur cycle is a typical sedimentary cycle. While sulphur occurs in high concentrations in localized deposits of the lithosphere (as FeS, S, and CuS), these sources are not usually located in the biosphere. However, sulphur atom has become an essential component of the biosphere, since it is involved in the formation of the chemical structure of living organisms. Protoplasm normally contains between 0.4 to 1.0 percent sulphur as organic sulphur compounds. In fact, sulphur provides rigidity to the protein. A protein cannot perform its functions unless it is folded and shaped in a peculiar way. This three dimensional structure is maintained by bonds between sulphur atoms that link one segment of a protein molecule to the other.

However low the concentration may be in the biosphere, sulphur has existed for millions of years on the surface of the planet earth in an oxidized form: as sulphates in soils, rocks, rivers, seas, and as sulphur oxides, a minor component of the atmosphere. The mobilization of sulphur begins with biological sulphate reduction.

In a typical cycle, plants take up sulphates and assimilate it as organic sulphur. This then moves through the food chain. Once plants and animals die, the organic sulphur is broken down and oxidized stepwise by a variety of bacteria to form sulphates that are taken up by plants and recycled **(figure 4.6.1)**.

4.6.2 Sulphur reserves

Most of the sulphur within the earth system is in the form of localized deposits, and not within the biosphere. Gypsum ($CaSO_4$) is an exception, but deposits of this mineral usually occur in arid and/or saline environments, which are not particularly favourable for the growth of organisms. **Table 4.6.1** gives an estimate of the world reserve of sulphur.

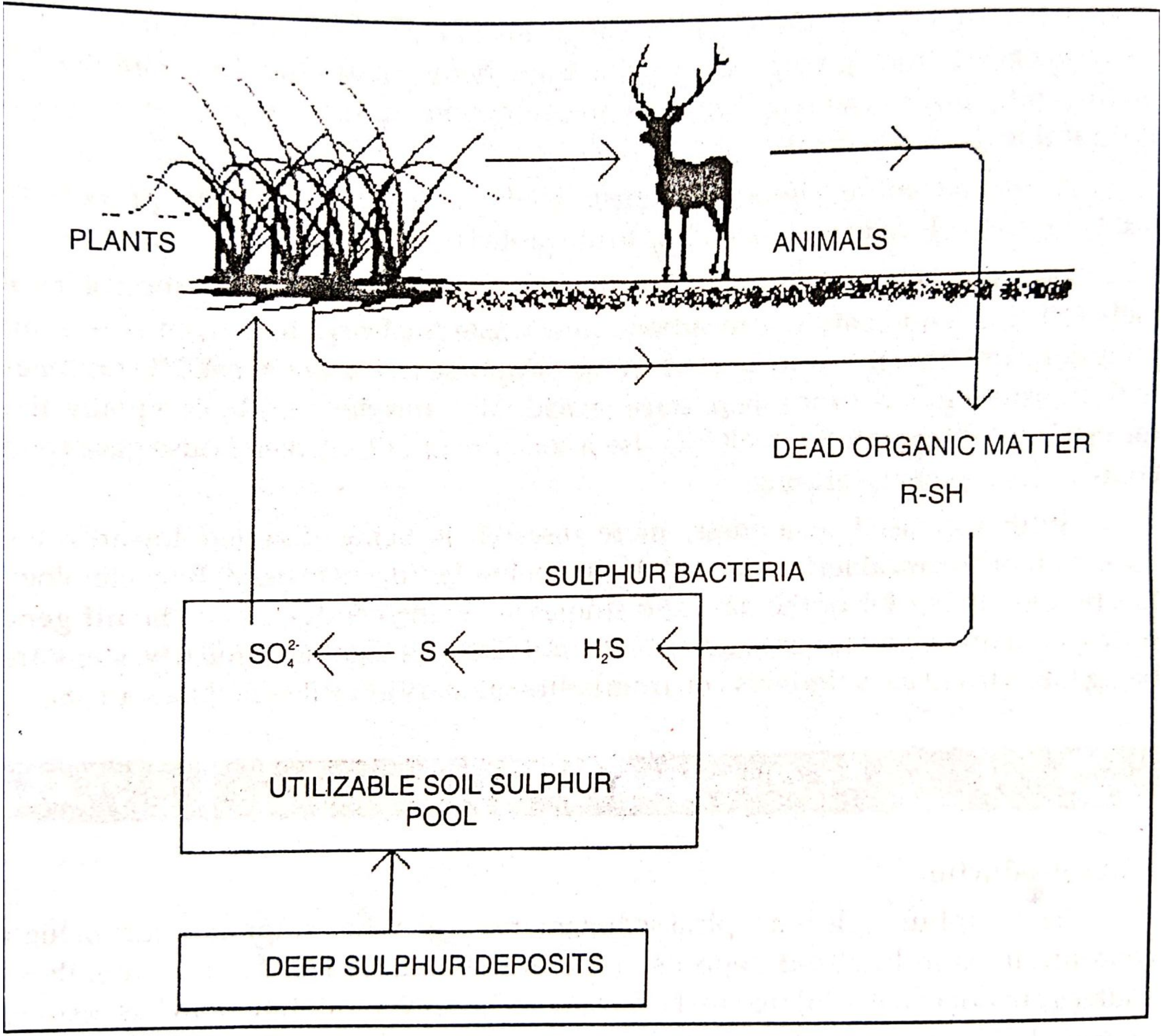

Figure 4.6.1 A simplified view of the sulphur cycle.

commodities required by man. Most of the sulphur extracted from these sources is used for the manufacture of fertilizers such as superphosphate, ammonium sulphate, and other compounds. This process directly feeds the biosphere with sulphur and amounts to about 0.03 billion tons.

The second process involves the transfer of sulphur from the reserves to the biosphere through man's consumption of coal, natural gas and petroleum, and to a lesser extent by the refining of base metal sulphide ores. Most of the sulphur released from these sources pass into the atmosphere in the form of gaseous sulphur dioxide. Annual estimates from this source is about 0.113 billion tons (Freney et al. 1983; Moller, 1984; Hameed and Dignon, 1988).

The third process, which adds sulphur to the biosphere is natural. Sulphur is emitted in various forms from geysers, springs and volcanoes, which are redistributed over the earth's surface by wind and water flow. Presumably most of this sulphur enters the biosphere. Sulphur is also released into the soil by the weathering of rocks containing sulphur minerals such as pyrites (FeS), galena (PbS), and gypsum ($CaSO_4$). Such processes are accelerated by biological activity, such as the opening of rock fissures by the roots of plants, especially trees. Weathering releases about 0.114 billion tons of sulphur annually into the biosphere.

4.6.4 Cycling of sulphur within the biosphere

In the typical cycling process, sulphur compounds (mainly as sulphates) present in the biosphere are taken up by green plants. The assimilation of sulphur by plants is termed as assimilatory sulphur reduction whereby the sulpates are reduced in steps (similar to nitrogen) to form hydrogen sulphide, which is then incorporated to form amino acids and proteins **(figure 4.6.2)**. This then moves through the food chain. When plants and animals die they are acted upon by various microorganisms, and the sulphur bacteria take up the task of releasing sulphur and recycling the element through the ecosystem.

Figure 4.6.4 The various sulphur bacteria involved in sulphur metabolism (a) *Chlorobium limicola*, a green photosynthetic sulphur bacteria with intracellular sulphur globules, (b) *Chromatium vinosum*, a purple photosynthetic sulphur bactria with intracellular sulphur globules, (c) *Desulfotomaculum nigrificans*, a sulphate reducing bacteria, (d) *Beggiatoa sp.*, a chemoorganotroph with intracellular sulphur granules (redrawn from Anderson, 1978).

these organisms require organic carbon for growth. Chemolithotrophic bacteria of the genus Thiobacillus oxidize sulphur as their energy source.

Desulfuromonas reduces elemental sulphur to sulphide at the expense of acetate

$$4S + NaOOC.CH_3 + 3H_2O \longrightarrow 4H_2S + NaHCO_3 + CO_2 \qquad \text{Eq. 4.6.3}$$

Beggiatoa and ***Thiothrix*** oxidizes hydrogen sulphide to elemental sulphur

$$2H_2S + O_2 \longrightarrow 2H_2O + S \qquad \text{Eq. 4.6.4}$$

Thiobacillus oxidizes elemental sulphur to sulphates

$$2/3S + O_2 + 3H_2O \longrightarrow 2/3\, SO_4^{2-} + 4/3\, H^+ \qquad \text{Eq. 4.6.5}$$

In the aquatic environment there is a closed cycling whereby organic sulphur is decomposed to release hydrogen sulphide in the deep anaerobic layers, while this is oxidized to elemental sulphur and sulphates by photolithotrophs in the aerobic layers **(figure 4.6.5)**.

4.6.5 Removal of sulphur from the biosphere

Removal of sulphur from the biosphere is accompanied by a gain in the sulphur reserves. Most of the processes that contribute to the removal of sulphur involve a combination of biological and physical factors.

(a) Formation of fossil fuels—Coal, natural gas and petroleum, which represent a large proportion of the sulphur reserves, are formed from biological material. The formation of fossil fuels however, also requires suitable physical conditions of temperature, pressure, time and anaerobic conditions.

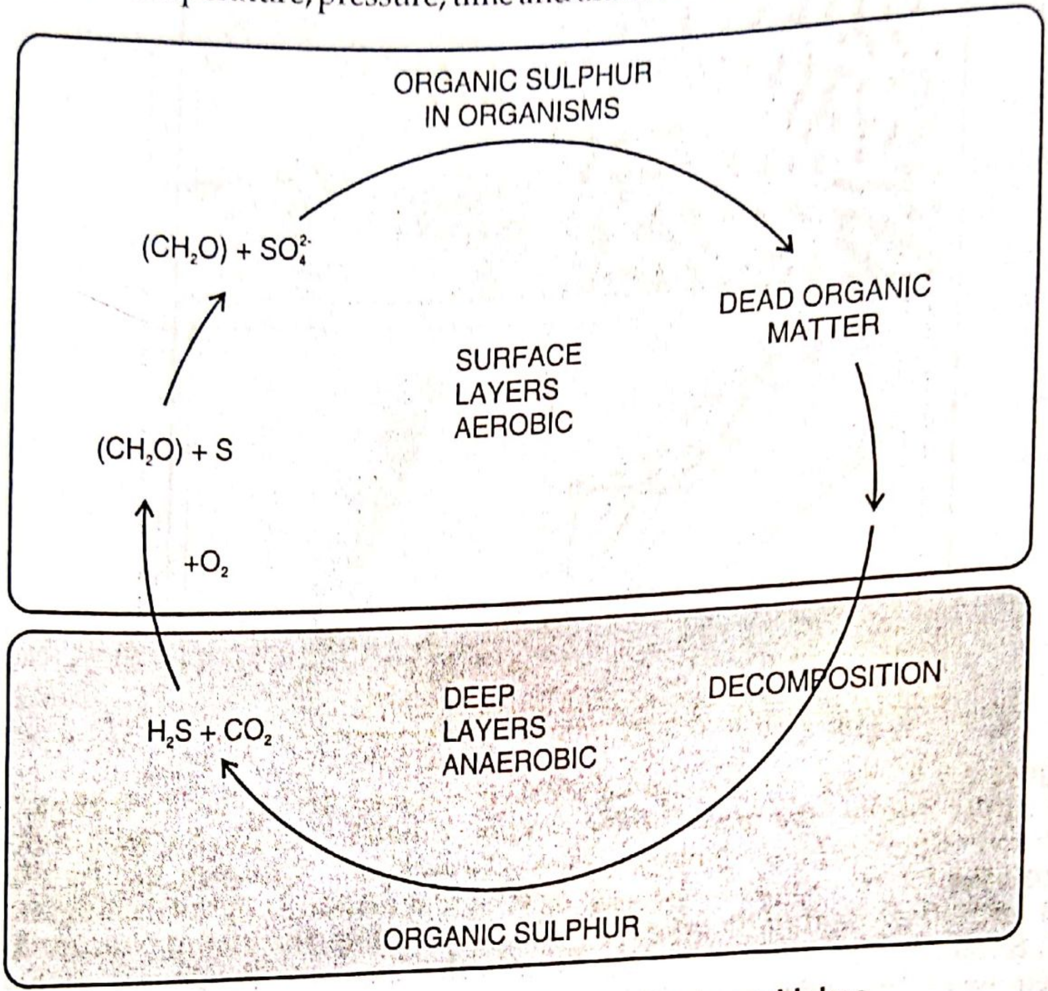

Figure 4.6.5 Cycling of sulphur in ponds and lakes.

(b) Formation of metal sulphides—Removal of sulphur from the biosphere also occurs in the formation of insoluble metal sulphides. This is aided by the dissimilatory sulphate reduction and desulphurylation processes. The sulphur thus released, reacts with cations of base metals to form the corresponding sulphides which, because of its low solubility precipitates out of solution, resulting in the removal of sulphur from the biosphere.

(c) Volatalization—Both the desulphurylating and dissimilatory sulphate reducing bacteria produce hydrogen sulphide that escapes into the atmosphere. Higher plants also volatilize sulphur. Some plants especially those of the family cruciferae volatilize large amounts of sulphur. However, this volatilization does not represent a loss of sulphur from the biosphere, as it is returned through precipitation.

4.6.6 Global sulphur budget

The global cycling of sulphur is quite complex and we do not have exact estimates as in the gaseous cycles. We have to consider the cycle at two levels: a large-scale slow cycle consisting of the cycling between the lithosphere, atmosphere, and hydrosphere by the physical processes such as, volatilization, volcanic action, sedimentation, weathering and precipitation. The second is the fast-moving biospheric cycle **(figure 4.6.6).** However as seen in table 4.6.2, the input of sulphur in the form of fertilizers and through industrial and automobile emissions has greatly disturbed the sulphur balance in all the spheres.

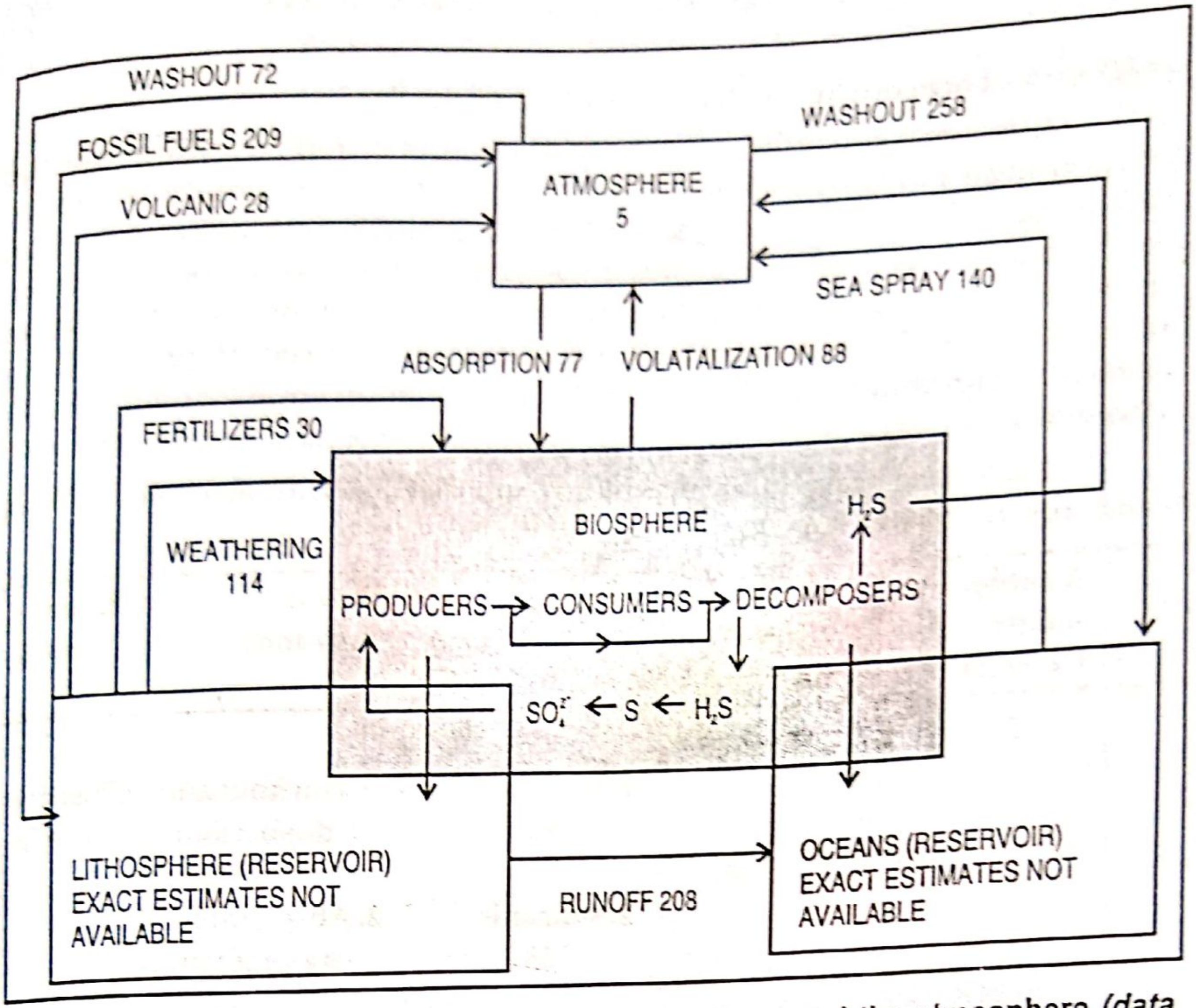

Figure 4.6.6 Transfer rates of sulphur to the biosphere and the atmosphere ***(data from Rodhe 1978; Cullis and Hirschler, 1980; Freney et al. 1983; and Wayne, 1986).***

Much of the sulphur that is introduced into the biosphere or the atmosphere ultimately passes to the sea as runoff water through rivers or as washout from the atmosphere through precipitation. However, the positive balance of about 58 million tons in the atmosphere is enough to create environmental problems. This is compounded by the additions to ground and surface waters.

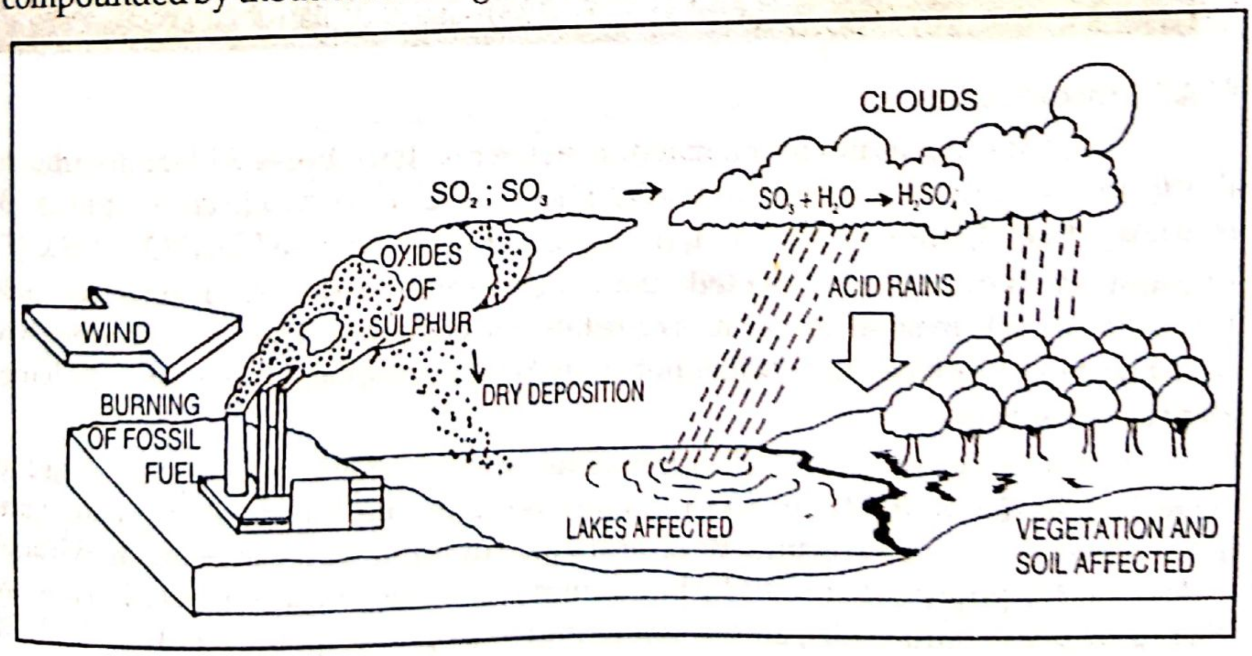

Figure 4.6.7 Acid rains. Burning of fossil fuel releases oxides of sulphur into the atmosphere. Some of it falls as dry deposition, while the rest drifts upwards and combines with moisture to form acids, which then falls as acid rains.

4.6.7 Impact of man on the sulphur cycle and its effect

Anthropogenic activity has been affecting the sulphur cycle considerably. With growing industrialization and increased use of fossil fuels, oxides of sulphur are produced, which pass into the atmosphere raising the concentration of the element and increasing its mobility. Details of the increase in the oxides of sulphur and its pollution aspects have been dealt in chapter 9. One of the important effects is the acid rains that affect both the terrestrial and aquatic environment (**figure 4.6.7**). Large amounts of sulphur are also being pumped into the biosphere in the form of fertilizers that accelerate the cycle and enhance the process of eutrophication (**see chapter 9**).

Table 4.5.4 The global Sulphur balance sheet (data from Rodhe 1978; Cullis and Hirschler, 1980; Freney *et al.* 1983; and Wayne, 1986).

Atmospheric Content (10^6 tons)	Residence time (days)	Return 10^6 tons	Withdrawal 10^6 tons	Balance 10^6 tons
5	2	1. Volatalization 88	1. Washout and deposition 330	Positive +58
		2. Volcanic 28	2. Absorption by vegetation 77	
		3. Fossil fuel 209		
		4. Sea spray 140		
Total		465	407	